

A chemical turnstile^{a)}

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A chemical turnstile is a device for transporting small, well-characterised doses of atoms from one location to another. A working turnstile has yet to be built, despite the numerous technological applications available for such a device. The key difficulty in manufacturing a chemical turnstile is finding a medium which will trap and transport atoms. Here we propose that ferroelastic twin walls are suitable for this role. Previous work shows that twin walls can act as two-dimensional trapping planes within which atomic transport is fast. We report simulations showing that a stress-induced reorientation of a twin wall can occur. This behaviour is ideal for chemical turnstile applications.

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There are many areas of technology in which the ability to deliver a chemical dose in small, well characterised quanta would be invaluable. Some examples can be found in biomedical technology, for the controlled release of a drug, as well as in nanotechnology for precision doping. For these applications we propose the idea of a chemical turnstile. The electronic equivalent, the electron turnstile, is already well known.¹ A schematic of a chemical turnstile is shown in Fig. 1. It possesses a trapping plane which captures diffusing ions. Diffusion within the plane occurs easily, but diffusion from within the plane into the bulk crystal is strongly inhibited. In the first stage of the turnstile operation (Fig. 1a) this trapping plane connects the upper and lower surfaces of the crystal. All the available sites within the plane will be occupied by dopant atoms: the number of such sites will define the dose quantum of the device. In the second stage of operation (Fig. 1b) the trapping plane is reoriented so that it connects the lateral surfaces. This allows the dopant atoms to diffuse

out into the host material. To build up the required dose, the turnstile can be repeatedly cycled through these two stages of operation.

A working chemical turnstile has yet to be built: the major obstacle is finding a material with a trapping plane which has the properties required. These are

- Two dimensional confinement to a small number of trapping sites.
- Fast exchange between trapping sites
- Controllable reorientation of the trapping plane

Previous experiments have shown that ferroelastic crystals possess the first two properties. Ferroelastic crystals exhibit anisotropic strains as a result of phase transitions—their microstructures show numerous twin walls between different variants of the low temperature phase.² These twin walls have a number of properties which make them very attractive as components in nanoscopic devices.³ Evidence of confinement within twin walls comes from direct measurements, simulations and from the observation of experimental effects which can be attributed to the trapping of atomic species by the wall. Examples of direct measurements showing confinement within twin walls include sodium diffusion experiments in tungsten oxide and ion microprobe measurements of anorthoclase twin walls.^{4,5} These measurements also showed that diffusion within the twin wall was significantly faster than bulk diffusion. Simulations showing chemical confinement within twin walls include simulations of generic models, sodium ions in quartz domain walls and trapping of oxygen vacancies within twin walls of calcium titanate and lead titanate.⁶⁻⁹ Indirect experimental evidence for the confinement of atoms within twin walls is given by, for example, the twin memory effect.^{10,11} The small width of twin walls, typically a few unit cells at most,^{12,13} shows that the number of trapping sites within the twin wall is small compared with the total number of sites in the crystal. Thus there is ample evidence that ferroelastic crystals satisfy the first two requirements. The third requirement is more difficult to fulfil. Experimental evidence from combined *in situ* X-ray diffraction and dynamical mechanical analysis shows that domain walls in lanthanum aluminate rotate in response to an applied stress.¹⁴ This, in itself,

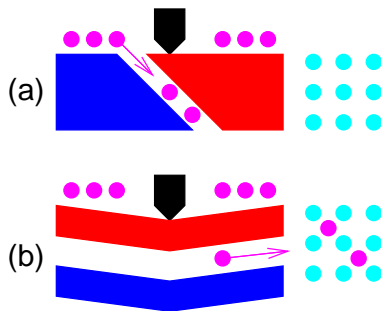


FIG. 1. Schematic of a chemical turnstile. In (a) atoms diffuse from the source into the trapping plane. In (b) the trapping plane is reoriented and the atoms allowed to diffuse out into the host material.

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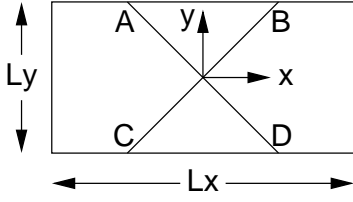


FIG. 2. Geometry used in equations 1 and 2. The lines AD and CB show the permissible twin wall orientations in the bulk material.

is not a sufficiently large orientational change to be useful in a chemical turnstile. Here we report simulations of the response of a twin wall to an applied bending stress which show a complete reorientation of the twin wall under a sufficiently large bending stress. This change is large enough for chemical turnstile applications.

To simulate the domain wall we used the method of finite elements, using the following free energy to describe the system

$$F = \frac{a}{2Q_0} (\epsilon_2 - Q_0^2)^2 + \frac{c_1}{2} \epsilon_1^2 + \frac{c_2}{2} \epsilon_{xy}^2 + \frac{g}{2} (\nabla \epsilon_2)^2 \quad (1)$$

where $\epsilon_1 = \epsilon_{xx} + \epsilon_{yy}$ and $\epsilon_2 = \epsilon_{xx} - \epsilon_{yy}$. The geometry of the system is shown in Fig. 2. The ground state consists of a single domain with $\epsilon_1 = 0$, $\epsilon_2 = \pm Q_0$ and $\epsilon_{xy} = 0$. Twin walls in the system should form 45° angles to the x and y axes. We will describe the details of the implementation of our model elsewhere.¹⁵ To this system we apply a bending stress of the form

$$\sigma_{xx} = \sigma_0 \frac{2y}{L_y} \quad (2)$$

Our simulations show that for small values of the bending stress there is a rotation of the twin wall, in agreement with experiments quoted in ref. 14. When the stress reaches a critical value, one twin is destabilised at the upper and lower surfaces. The twin wall is forced to disconnect from these surfaces and to follow a path confined to the low stress region in the centre of the crystal, as shown in Fig. 3. In part (a) the wall is shown in its stress free configuration. The wall is rotated away from the ideal 45° orientation due to the finite size of the simulation. In (b) a bending stress small compared to the critical bending stress has been applied, and the domain wall has rotated. In part (c) a stress larger than the critical bending stress has been imposed and the twin wall is no longer stable on the upper and lower surfaces. These results show that ferroelastic twin walls also fulfil the final requirement needed to work in a chemical turnstile.

For chemical turnstile applications, one important question is, how much material will be transported in a single cycle of the turnstile? i.e. what is the dose quantum? Consider a crystal of cross-section $2 \mu\text{m}$ by $0.2 \mu\text{m}$. Take the unit cell size to be of the order of 0.5 nm and assume one dopant site per unit cell. Finally, assume that the twin wall width is approximately one unit cell. This gives a dose quantum of the order of 10^5 atoms. A device of nanoscopic size would reduce the dose quantum even further to give a truly atomic resolution.

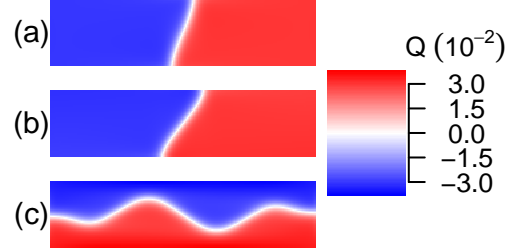


FIG. 3. Wall trajectories under different bending stresses. In (a) there is no bending stress, in (b) a small bending stress has been applied, and in (c) the bending stress is larger than the critical value.

It seems likely that, in the near future, ferroelastic twin walls will be used in a number of nanotechnological applications.³ These will use both the static properties of the twin walls e.g. exploiting the confined superconductivity of WO_3 walls¹⁶ and their dynamic properties, such as the reorientation under an applied bending stress described here. The chemical turnstile is an important example of the latter type of application.

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